

Critical role of the external bias in improving the performance of polymer solar cells with a small molecule electrolyte interlayer†

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A small-molecule electrolyte based on the popular ethylene diamine tetraacetic acid (EDTA-N) is introduced as an efficient cathode interlayer in inverted polymer solar cells, helping to deliver power conversion efficiency over 9%. The strong dependence of device performance on the external bias suggests that the ion motion plays a critical role in improving the performance of devices with electrolyte interlayers.

Bulk-heterojunction (BHJ) polymer solar cells (PSCs) have attracted much attention due to their advantages of flexibility, light weight, low cost and ease of large area fabrication through roll-to-roll printing.¹⁻⁵ The typical architecture of PSCs is a sandwich structure, where the photoactive materials are sandwiched between the anode and the cathode. Since charge injection/extraction can significantly affect the device performance, interfacial modification between organic materials and electrodes has become a crucial issue.^{6,7} Therefore, much effort has been focused on developing novel interfacial materials and understanding the corresponding device performance.⁸⁻¹⁶

Among various interfacial materials, conjugated electrolytes containing a π -delocalized backbone with pendant charge groups capable of ionization have attracted substantial interest due to their applications in organic electronic devices.^{9,12,17-21} Their solubility in polar solvents allows fabrication of multilayer devices without interface mixing through the solution processed approach. Very recently, we demonstrated efficient electron injection in polymer light-emitting diodes (PLEDs) by using quaternary ammonium small-molecule electrolytes

without any π -delocalized backbone as interlayers.¹⁵ This work indicated that the ionic part of electrolyte is crucially important for charge injection and that the π -delocalized structure is not absolutely necessary for the charge-injection function.¹⁵

However, in PSCs, the neutral precursors of the organic electrolytes (without any ionic parts), such as poly[(9,9-bis(3'-(*N,N*-dimethylamino)propyl)-2,7-fluorene)-*alt*-2,7-(9,9-dioctylfluorene)] (PFN), were reported to deliver an impressive power conversion efficiency (PCE) of 9.2%.¹⁸ In contrast, the electrolyte interlayers in PSCs usually give a relatively low efficiency compared with their neutral precursors, and the reason behind it is not clear yet.^{11,18,22} This also opens up a fundamental question: for the electrolyte interlayers in PSCs, does the ionization help the charge collection (like in the case of PLEDs), or does it merely change the solubility? The difference between the precursor and the corresponding electrolyte lies in the mobile ions. For PLEDs, it has been identified that ion migration within the electrolytes plays an important role in improving the device performance.²³⁻²⁵ The voltage applied during the PLED measurement is usually higher than 4 V, which is large enough to drive the ion migration within a short time, while for PSCs, the scan voltage range is generally less than 1.5 V. We hypothesize that the small applied bias in PSC measurements might make it difficult to observe the effect of ion arrangement on the device performance. In order to separate the effect of the conjugated backbone and that of the ionic section in the electrolytes on the PSC performance, it is preferable to use electrolytes without any π -delocalized backbone, *e.g.* small-molecule electrolytes (SMEs). Actually, SMEs offer further intrinsic advantages over conjugated polyelectrolytes. They are synthesized easily without complex C-C coupling and polymerization reactions, are monodisperse in nature with well-defined chemical structures, and are synthetically well-reproducible.^{15,26,27}

Here, we demonstrate successful applications of a small molecule ethylene diamine tetraacetic acid derivative (EDTA-N, Fig. 1) as the cathode interlayer in inverted PSCs. By applying a

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bias prior to the device measurement, the power conversion efficiency (PCE) could be significantly increased from $\sim 6\%$ to 9.03%, which is among the highest PCEs for single-junction PSCs. The device performance is found to strongly depend on the size, direction and duration of pre-bias. For the first time, to the best of our knowledge, the dependence of PSCs with SME buffer layers on the external bias is systematically investigated, providing insight into further improvement of device performance exceeding 10%.

EDTA is well-known as a hexadentate ligand and chelating agent. EDTA-N was obtained through the reaction of EDTA and triethylamine (details in the Experimental section). EDTA-N is highly soluble in methanol and not soluble in chlorobenzene due to the existence of ions, making it an ideal buffer layer material for the inverted PSC configuration (Fig. 1). The EDTA-N interlayer was prepared by spin-coating the solution (1 mg mL^{-1} in methanol) at 4000 rpm on indium tin oxide (ITO) substrates. Low bandgap polymers thieno[3,4-*b*]thiophene/benzodithiophene (PTB7) and phenyl C71-butyric acid methyl ester (PC₇₁BM) were used as photoactive materials. For comparison, conventional devices with the configuration of ITO/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/PTB7:PC₇₁BM/Ca/Al were also fabricated under the same conditions.

Table 1 summarizes the device parameters. The conventional structured devices exhibit a typical PCE of 6.90% (the highest PCE of 7.14%).²⁸ And the inverted PSCs without any interlayer show rather inferior performance (an average PCE of 0.72%) due to the high work function of the bare ITO. After EDTA-N is introduced as the cathode interlayer, the PCE significantly increases to 6.2%, indicating successful surface

modification of the ITO by EDTA-N. However, this value is still lower than that of the conventional device, mainly due to the inferior open circuit voltage (V_{oc}) and fill factor (FF).

In order to examine the potential effect of the external bias (and ion migration) on the device performance, we directly apply a bias on the devices prior to the device measurement (MoO₃/Al is biased as the positive electrode and ITO/EDTA-N as the negative electrode). Note that all the bias was applied on devices under dark conditions to avoid the possible existence of light-soaking effects as possible. When a 4 V bias is applied for 15 s, the PCE could significantly increase to 9.03%, which is among the highest PCEs for single-junction PSCs.¹⁸ We systematically investigate the relationship between the bias and the device performance, as shown in Fig. 2. When a small 0.5 V bias is applied, the device performance keeps increasing with increasing bias time. After ~ 480 s, the PCE and V_{oc} reach a saturated value (Table S1[†]). When the applied bias is increased to 1 V, it takes only ~ 300 s to reach the saturated value (Table S2[†]). When a 2 V bias is applied, it takes only 150 s for the initial V_{oc} (0.673 V) and PCE (6.67%) to increase to 0.745 V and 8.62% (Table S3[†]). And if we continue to increase the applied bias to 4 V, just 5 s is already enough for the PCE (6.32%) to increase to 8.38% (Table S4[†]). The higher pre-bias not only shortens the saturation time but also improves the saturated PCE (from 7.89% at 0.5 V to 9.03% at 4 V), as shown in Fig. 2, indicating that the pre-bias played a major role in the performance improvement and the effect of light-soaking could be ignored. Compared with the fresh device, the V_{oc} increases from about 0.66 V to 0.75 V after pre-bias (Table 1). And the FF also increases from less than 60% to $\sim 70\%$. As a result, about 45% improvement in PCEs (from 6.20% to 8.93%) is achieved by simply applying a bias for a short time. The statistical comparison of the device performance data before and after pre-bias is shown in Fig. S1.[†] In addition, we also examine the J - V characteristics under dark conditions after the external bias. As shown in Fig. S2,[†] with increasing bias time (biased at 2 V), the injection current gradually increases, which indicates improved interface modification, consistent with the enhanced photovoltaic performance.

Since a bias as low as 1 V already helps to improve the device performance, we expect that the PCE could also be improved by repeated measurements (as a result of the bias during measurements). A typical fresh device with an EDTA-N interlayer shows only moderate performance with a V_{oc} of 0.686 V, a

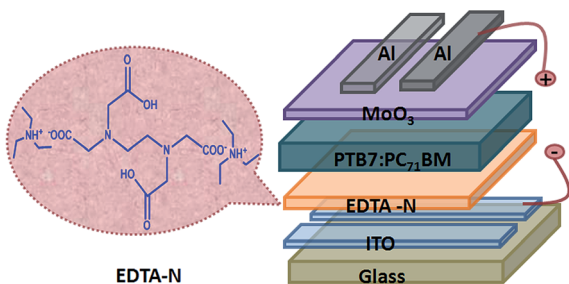


Fig. 1 Chemical structure of EDTA-N and device configuration used in our work.

Table 1 The photovoltaic parameters of conventional and inverted PSCs with or without the cathode interlayer

No.	V_{oc}/V	$J_{sc}/\text{mA cm}^{-2}$	FF/%	PCE/%	$R_s/\Omega \text{ cm}^2$
Conventional	0.718	14.72	65.2	6.90 ± 0.13	10.8
Bare ITO	0.162	13.38	32.5	0.72 ± 0.25	7.5
EDTA-N ^a	0.662	16.61	56.4	6.20 ± 0.28	13.5
EDTA-N-V ^b	0.746	16.75	71.4	8.93 ± 0.07	4.7

^a The parameters of fresh devices. ^b The parameters of devices after pre-bias. All the parameters are average values among a batch of 8 devices.

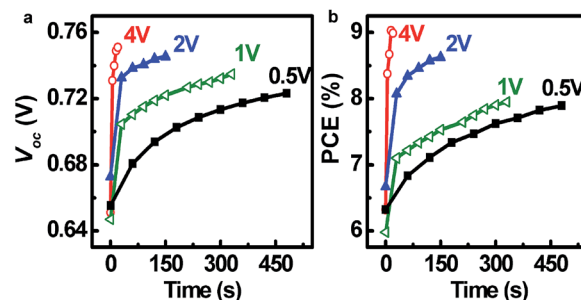


Fig. 2 The variation of V_{oc} and PCE with pre-bias time for the device with the EDTA-N interlayer.

J_{sc} of 16.65 mA cm^{-2} , a FF of 53.3% and a PCE of 6.09% (Fig. 3a and b). When we continue measuring the same device with a scan bias from -1.5 V to 1.5 V , the PCE will be improved to 6.72% due to the apparently enhanced V_{oc} (0.709 V) and FF (56.7%). With increasing measurement times, the PCE continues increasing slowly until it reaches a saturated value. After 10 times continuous measurements, the PCE reaches 7.71% with a high V_{oc} of 0.728 V and a FF of 63.2% (Table S5†).

All the above results demonstrate that the external bias plays a critical role in improving the device performance. It implies that the measurement conditions could affect the device performance, but no report on PSCs with electrolyte interlayers has paid attention to this effect so far. We further vary the scan voltage range during measurements and the results are shown in Fig. 3c and d. When we measure the device from -1.5 V to 1.5 V , the PCE is 6.41% with a V_{oc} of 0.668 V and a FF of 58.8%. However, when we measure the device from 4 V to -1.5 V , the PCE greatly increases to 8.19% with a high V_{oc} of 0.729 V and a FF of 68.5% (Table S6†). Interestingly, when we switch the scan range to measure the device from -4 V to 1.5 V , only a PCE of 5.88% is obtained, due to the obviously decreased V_{oc} of 0.657 V and a FF of 55.5%. The detailed results are presented in Table S6.† Obviously, the scan range of the measurement could also affect the device parameters. It indicates the importance of specifying the measurement conditions since it will result in different device performances.

To further understand the origin of the external bias on the PSC performance, we study the current density (J) response of the EDTA-N based PSCs over time under different constant external biases under dark conditions. As shown in Fig. 4, the temporal evolution of J changes with the size of the external bias. Under 0.5 V bias, the J gradually decreases with time. A similar phenomenon has been observed in light-emitting electrochemical cells (LECs) and was ascribed to the electric double layer formation (as a result of ion motion).^{29,30} We suspect that similar mechanisms are involved here, considering the ionic

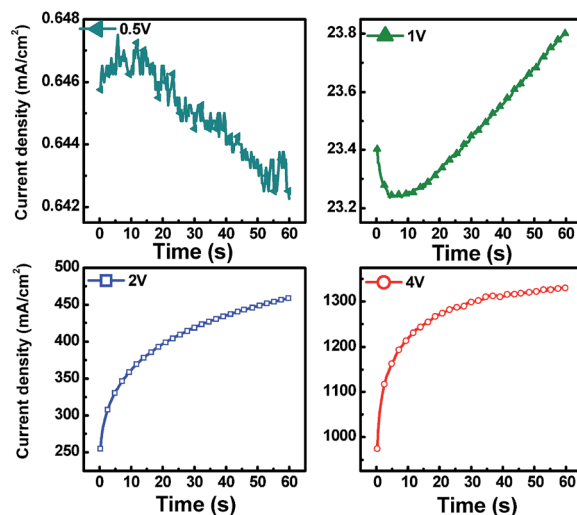


Fig. 4 The J response over time under different biases (in the dark).

nature of the electrolytes. The ion reorientation or motion in the EDTA-N interlayer forms an electrical double layer. This electric double layer results in an extra internal electric field, which is opposite to the external electric field, thus leading to the decrease of J .^{29,30} In order to further examine this hypothesis, we increase the bias to 1 V , which is comparable to the built-in electric field of PSCs. Under 1 V , the J decreases first and then starts to increase slowly. This result agrees well with the electric double layer formation hypothesis. After the electric double layer is formed, the injection barrier is decreased, which is responsible for the increase of J . A similar phenomenon was also observed in PLECs.²⁹⁻³¹ For devices under larger bias (2 V or 4 V , for example), the initial decrease of J disappears. For 2 V or 4 V biased devices, the external electrical field is much higher than the built-in electric field of PSCs, and hence the formation of the electric double layer is much faster, making this process difficult to observe directly. Instead, a much more rapid and significant increase of J over time is observed. If we define the time at which J approaches the saturated value as the response time, the response time is about 20 s for 4 V and 60 s for 2 V , respectively. It is consistent with time to reach the saturation efficiency shown in Fig. 2. All our results are similar to those observed for LECs,²⁹⁻³¹ where the ion migration under the electric field is widely accepted as the key operation mechanism. And the ion reorientation or migration picture also explains our results very well.

Based on the above analysis, we propose a diagram explaining the critical role of the electric field in improving the device performance with electrolyte interlayers (Fig. 5). Upon the application of an external bias, the anions (COO^-) accumulate at the EDTA-N/ PC_{71}BM :PTB7 interface and cations accumulate at the ITO/EDTA-N interface (Fig. 5b). The redistribution/reorientation will lead to the introduction of an extra electric field. The direction of the electrical field is the same as that of the built-in electrical field (Fig. 5b). On the one hand, this is helpful to improve charge collection. On the other hand, it can increase the whole built-in electrical field of the devices

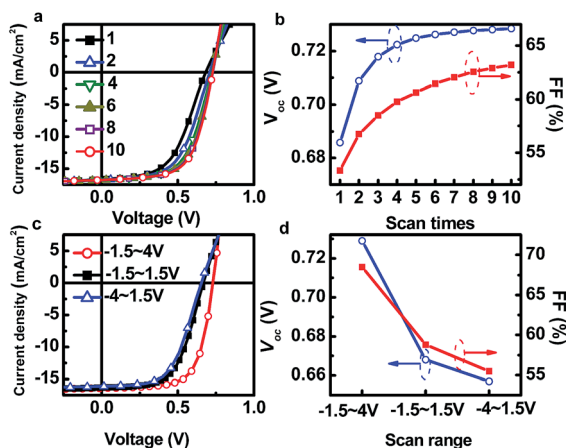


Fig. 3 (a) The variation of J - V curves with the measurement times (the scan voltage range is from -1.5 V to 1.5 V); (b) the V_{oc} and FF variations corresponding to (a); (c) the J - V curves with different scan ranges; (d) the V_{oc} and FF variations corresponding to (c).

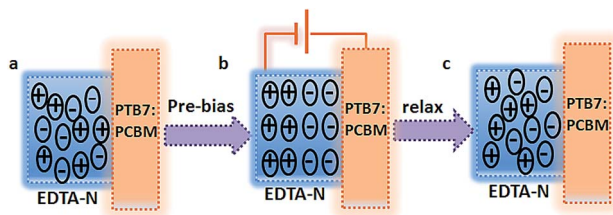


Fig. 5 Schematic illustration of ion distribution and motion in EDTA-N: (a) before bias; (b) after bias; (c) relaxation.

and effectively reduce the recombination. This is consistent with the significant improvement of V_{oc} and FF after pre-bias. In addition, the anion accumulation at EDTA-N/PC₇₁BM:PTB7 may also induce the doping of fullerenes, thus improving the efficiency of electron collection.^{32–35} The higher pre-bias will lead to faster ion redistribution/reorientation. As a result, it takes a much shorter time for the device to reach the saturated value. And under the higher pre-bias condition, the number of separated ions is higher and the resulting built-in electrical field is larger. That is why the PCE of the devices with 4 V (9.03%) is significantly higher than that of 0.5 V (7.89%). In the repeated measurement process, with the increasing test times, the ion distribution becomes increasingly beneficial to the device performance. As a result, the device performance keeps improving with increasing measurement times and finally reaches a saturated value.

In order to further back up our explanation, we replace EDTA-N with a neutral polymer interlayer (PFN-4, Fig. S3†). Based on our analysis, for PSCs with the interlayer containing no ions, the device performance is not supposed to change after pre-bias treatment. Indeed, we find that the devices with the PFN-4 interlayer show almost the same performance under 4 V bias treatment as expected (Table S7†). This control experiment further confirms the dominant role of ion motion in device performance with electrolyte interlayers.

Since the device performance is significantly affected by the ion distribution/reorientation, an issue concerning the practical application is how stable the device is. We recorded the performance of a typical device with an optimized PCE of 8.99% after pre-bias. The device PCE decreases to 8.05% with a slightly decreased V_{oc} of 0.740 V and a FF of 66.3% after being stored in the glove box (filled with Ar) for 98 h. However, when a bias (4 V) is applied for 20 s, the PCE is recovered to 8.85% with an obviously improved V_{oc} of 0.758 V and a FF of 71.1%. We note that the PCE after being stored for a long time (98 h) is still much higher than that of the fresh devices, which implies that the ion motion is quite slow or that the permanent dipole induced by molecule rearrangement through the external electrical field still exists. As to the about 10% loss in PCE (8.05% versus 8.85% if ignoring the device degradation), it may be caused by the ion relaxation²⁴ as shown in Fig. 5c. In addition, the stability of the devices and surface morphology were also studied as shown in Fig. S4 and S6.† The EDTA-N coated ITO showed a rather smooth surface with a root mean square (RMS) of 2.58 nm and the corresponding devices exhibited a much

better stability than that of conventional structured devices under the same conditions (Fig. S4†). These results indicate that apart from the enhanced PCE, a better device stability could also be obtained by using EDTA-N as the interfacial material.

Conclusions

In summary, a small molecule EDTA derivative (EDTA-N) has been investigated as the cathode interlayer in inverted PSCs. The performance is found to strongly depend on the external bias treatment. By applying an external bias prior to the measurement for a short time, the PCE could be impressively increased from ~6% to 9.03%, which is among the highest PCEs for PSCs with small molecule electrolyte interlayers. We further demonstrate that the device performance also significantly depends on the measurement conditions, such as the scan range, scan history, *etc.* This indicates that a “poor” or “excellent” electrolyte interlayer material is defined not only by the material itself but also by the measurement conditions, especially for the PSCs with ion-containing interlayers. The ion motion is suggested to be responsible for the device improvement under the external electric field conditions. This work has demonstrated promising applications of SMEs as well as conjugated polyelectrolytes for PSC interlayers and it provides new routes to achieve 10% PCE for PSCs.

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